

Title: **EMULSIFIED WATER-BLENDED FUEL COMPOSITIONS**

This application is a continuation in part of U.S. Application No. 09/152,852, filed September 14, 1998, and also a continuation in part of U.S. application Serial No.

5 09/390,925, filed on September 7, 1999, that is a continuation in part of U.S. application Serial No. 09/349,268, filed July 7, 1999, that is a continuation in part of 09/483,481. Each of the disclosures of the prior applications is incorporated herein by reference, in their entirety.

BACKGROUND OF THE INVENTION

10 The present invention relates to emulsified water-blended fuel compositions, more particularly to water-blended fuel compositions containing a liquid fuel, water, an emulsifier, and an amine salt which may function as an emulsion stabilizer or combustion modifier. In one embodiment of the invention, the composition further comprises an organic cetane improver, and in one embodiment an antifreeze.

DESCRIPTION OF THE RELATED ART

15 Internal combustion engines, especially diesel engines using a mixture of water and fuel in the combustion chamber can produce lower NO_x, hydrocarbon and particulate emissions per unit of power output. Water is inert toward combustion, but acts to lower peak combustion temperatures that result in less NO_x formation. Exhaust Gas Recirculation
20 (EGR) works on the same principle; that is, inert materials tend to lower peak combustion temperatures and hence reduce NO_x. Water can be separately injected into the cylinder, but hardware costs are high. Water can also be added to the fuel as an emulsion. However, emulsion stability has historically been a problem.

It would be advantageous to provide a water-blended fuel composition that has
25 improved emulsion stability. The present invention provides such an advantage.

U.S. Patent 5,669,938, Schwab, September 23, 1997, discloses a fuel composition which consists of (i) a water-in-oil emulsion comprising a major proportion of a hydrocarbonaceous middle distillate fuel and about 1 to 40 volume percent water, (ii) a CO
30 emission, and particulate matter emission reducing amount of at least one fuel-soluble organic nitrate ignition improver, and optionally containing (iii) at least one component selected from the group consisting of di-hydrocarbyl peroxides, surfactants, dispersants,

organic peroxy esters, corrosion inhibitors, antioxidants, antirust agents, detergents, lubricity agents, demulsifiers, dyes, inert diluents, and a cyclopentadienyl manganese tricarbonyl compound.

European Patent EP 0 475 620 B1, Sexton et al., August 11, 1995, disclose a diesel fuel composition which comprises: (a) a diesel fuel; (b) 1.0 to 30.0 weight percent of water based upon said diesel fuel; (c) a cetane number improver additive, present in an amount up to, but less than, 20.0 weight percent based upon said water, said additive being selected from an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and (d) 0.5 to 15.0 wt. % based on the diesel fuel of a surfactant system comprising (i) one or more first surfactants selected from surfactants capable of forming a lower phase microemulsion at 20°C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said first surfactant being an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of a C₉-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene oxide groups; and (ii) one or more second surfactants selected from surfactants capable of forming an upper phase microemulsion at 20°C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said surfactant being an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of C₉-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing less than 6 ethylene oxide groups; the said first and second surfactants being present in a weight ratio which forms with components (a), (b) and (c) a single phase translucent microemulsion.

European patent publication EP 0 561 600 A2, Jahnke, September 22, 1993, discloses a water in oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-supplying component (such as ammonium nitrate); a continuous organic phase comprising at least one carbonaceous fuel; and a minor emulsifying amount of at least one emulsifier made by the reaction of:

(A) at least one substituted succinic acylating agent, said substituted acylating agent consisting of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene, said acylating agents being characterized by the presence within

their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups, and

(B) ammonia and/or at least one amine.

U.S. Patent 5,047,175, Forsberg, September 10, 1991, discloses salt compositions which comprise: (A) at least one salt moiety derived from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, and (A)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; (B) at least one salt moiety derived from (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of up to about 18 carbon atoms, and (B)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; said components (A) and (B) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group. These salt compositions are disclosed to be useful as emulsifiers in water-in-oil explosive emulsions, particularly cap-sensitive water-in-oil emulsions.

U.S. Patent 4, 708,753, Forsberg, November 24, 1987, discloses a water-in-oil emulsion comprising (A) a continuous oil phase; (B) a discontinuous aqueous phase; (C) a minor emulsifying amount of at least one salt derived from (C)(I) at least one hydrocarbyl-substituted carboxylic acid or anhydride, or ester or amide derivative of said acid or anhydride, the hydrocarbyl substituent of (C)(I) having an average of from about 20 to about 500 carbon atoms, and (C)(II) at least one amine; and (D) a functional amount of at least one water-soluble, oil-insoluble functional additive dissolved in said aqueous phase; with the proviso that when component (D) is ammonium nitrate, component (C) is other than an ester/salt formed by the reaction of polyisobutenyl ($M_n=950$) succinic anhydride with diethanolamine in a ratio of one equivalent of anhydride to one equivalent of amine.

U. S. Patent 3,756,794, Ford, September 4, 1973, discloses an emulsified fuel composition consisting essentially of (1) a major amount of a hydrocarbon fuel boiling in the

range of 20-400°C as the disperse phase, (2) 0.3% to 5% by weight of an emulsifier, (3) 0.75% to 12% by weight water, (4) 0.3% to 0.7% by weight of urea as emulsion stabilizer and (5) 0.3% to 0.7% by weight of ammonium nitrate.

SUMMARY OF THE INVENTION

5 This invention relates to an emulsified water-blended fuel composition comprising:

(A) about 50% to about 99% by weight of a hydrocarbon fuel;

(B) about 1% to about 50% by weight of water;

(C) about 0.1% to about 10% of a minor emulsifying amount of at least one fuel-soluble salt comprised of (I) a first acylating agent, said first acylating agent having at least one hydrocarbyl substituent of about 20 to 500 carbon atoms and a molecular weight (Mn) in the range of about 500 Mn to 10,000 Mn, (II) a second acylating agent, said second acylating agent selected from the group consisting of monocarboxylic agents, polycarboxylic agents, dicarboxylic agents and combinations thereof; and wherein said second acylating agent has at least 1 hydrocarbyl substituent of up to about 35 carbon atoms and reacting said carboxylic acylating agents (I) and (II) with (III) an ammonia or an amine to form a salt; and

(D) about 0.001% to about 15% by weight of the water-soluble salt distinct from component (C).

In one embodiment, the composition further comprises at least one organic cetane improver; and in one embodiment, at least one antifreeze, and in one embodiment at least one alcohol.

In the preferred embodiment, this invention relates to an emulsified water-blended fuel composition comprising: (A) a hydrocarbon fuel; (B) water; (C) a minor emulsifying amount of at least one fuel-soluble salt comprised of (I) a first acylating acid, said first acylating acid having at least one hydrocarbyl substituent of about 20 to about 500 carbon atoms and a molecular weight (Mn) of about 500 to 10,000 (II) a second acylating agent having at least one hydrocarbyl substituent of up to about 35 carbon atoms, and reacting said acylating agents (I) and (II) forming a salt with (III) ammonia or an amine; and (D) about 0.001% to about 15% by weight of a water-soluble salt distinct from component (C). In the preferred embodiment the first acylating agent is a polycarboxylic acid and the second acylating agent is a monocarboxylic acid.

The water-blended fuel composition is comprised of droplets having a mean diameter of 1.0 micron or less. In one embodiment the mean droplet size is less than about 0.95 micron, in one embodiment less than about 0.8 micron, and in one embodiment less than about 0.7 micron. In one embodiment the mean droplet size is in the range of about 0.1 to about 0.95, in one embodiment about 0.1 to about 0.7 micron, in one embodiment 0.1 to about 0.5 micron. In one embodiment, the droplet size is in the range of about 1.0 to about 0.5 micron.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

(3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every 10 carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

The term "hydrocarbylene group" refers to a divalent analog of a hydrocarbyl group. Examples of hydrocarbylene groups include ethylene ($-\text{CH}_2\text{CH}_2-$), propylene (both linear and branched), and 2-octyloxy-1,3-propylene ($-\text{CH}_2\text{CH}(\text{OC}_8\text{H}_{17})\text{CH}_2-$).

The phrase "reactive equivalent" of a material means any compound or chemical composition other than the material itself that reacts or behaves like the material itself under the reaction conditions. Thus for example, reactive equivalents of carboxylic acids include acid-producing derivatives such as anhydrides, acyl halides, and mixtures thereof unless specifically stated otherwise.

The term "lower" when used in conjunction with terms such as alkyl, alkenyl, and alkoxy, is intended to describe such groups that contain a total of up to 7 carbon atoms.

The term "water-soluble" refers to materials that are soluble in water to the extent of at least one gram per 100 milliliters of water at 25°C.

The term "fuel-soluble" refers to materials that are soluble in fuel (gasoline or diesel) to the extent of at least one gram per 100 milliliters of fuel at 25°C. It also refers to materials that end up mostly in the fuel phase when a mixture of a certain quantity of the material and equal volume of fuel and water are mixed together, leaving the water phase substantially (greater than 90%) free of the material.

In one embodiment of the present composition, the components are mixed together to form a water-in-fuel emulsion with the hydrocarbon fuel being the continuous phase, and water being the discontinuous phase dispersed in the hydrocarbon fuel phase.

The components of the emulsified water-blended fuel composition are described in detail hereunder.

The Hydrocarbon Fuel (A)

The liquid hydrocarbon fuel comprises hydrocarbonaceous petroleum distillate fuel, non-hydrocarbonaceous materials that include but are not limited to oils, liquid fuels derived from vegetables, rapeseed, ethanol, liquid fuels derived from minerals and mixtures thereof and combinations thereof. Liquid hydrocarbon fuel may be any and all hydrocarbonaceous petroleum distillate fuels including but not limited to gasoline, diesel fuel, fuel oil, biodegradable fuels, biodiesel fuels and the like. The liquid hydrocarbon fuels comprising non-hydrocarbonaceous materials include but are not limited to alcohols, such as methanol, ethanols and the like; ether such as diethyl ether, methyl ethyl ether and the like; liquid fuels derived from vegetable sources such as corn, alfalfa, rapeseed, and mineral sources such as shale, coal and the like. Liquid hydrocarbon fuels also include mixtures of one or more hydrocarbonaceous and one or more non-hydrocarbonaceous materials. Examples of such

mixtures are combinations of gasoline and ethanol, a diesel fuel and ether, gasoline and a biodegradable fuel, diesel fuel and a biodegradable fuel, and gasoline or diesel fuel with a renewable resource additive or fuel.

5 The hydrocarbon fuel contains in one embodiment biodegradable fuel, biodegradable fuel additive, renewable resource, additive renewable resource or mixtures thereof in the range of about 0.1% to about 100%, in another embodiment about 2% to about 75%, in another embodiment about 10% to about 50%, in another embodiment about 2% to about 15%, in another embodiment about 100%.

10 In one embodiment one component of the composition of this invention is a hydrocarbon fuel boiling in the gasoline or diesel range. Motor gasoline is defined by ASTM Specifications D-439-89. It comprises a mixture of hydrocarbons having an ASTM boiling point of 60°C at the 10% distillation point to about 205°C at the 90% distillation point. The fuel may contain alcohols, esters, biodegradable materials and combinations thereof. In one embodiment, the fuel is a chlorine-free or low-chlorine gasoline characterized by a chlorine content of no more than about 10 ppm. In one embodiment the gasoline fuel has a sulfur content of about up to about 0.05% by weight as determined by the test method specified in ASTM D 2622-87.

15 In one embodiment the diesel fuels that are useful with this invention can be any diesel fuel. They include those that are defined by ASTM Specification D396. In one embodiment the diesel fuel has a sulfur content of up to about 0.05% by weight (low-sulfur diesel fuel) as determined by the test method specified in ASTM D 2622-87 entitled "Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry." Any fuel having a boiling range and viscosity suitable for use in a diesel-type engine can be used. These fuels typically have a 90% point distillation temperature in the range of about 300°C to about 390°C, and in one embodiment about 330°C to about 350°C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40°C. These diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D 975 entitled "Standard Specification for Diesel Fuel Oils." These diesel fuels may contain alcohols, esters, biodegradable materials and mixtures thereof. In one embodiment, the diesel fuel is a chlorine-free or low-chlorine diesel fuel characterized by a chlorine content of no more than

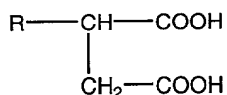
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about 10 ppm. In one embodiment the diesel fuel has a sulfur content of about up to about 0.05% by weight as determined by the test method specified in ASTM D 2622-87.

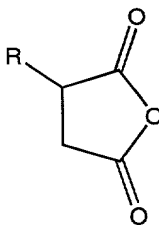
The liquid hydrocarbon fuel present in the emulsified water-blended fuel is at a concentration in the range of about 50% to about 95% by weight, in one embodiment about 5 60% to about 95% by weight, in one embodiment about 65% to about 85% by weight, and in one embodiment about 80% to about 90% by weight of the emulsified water-blended fuel.

The Acylating Agent (C)(I)

The acylating agent (C)(I) is a hydrocarbyl-substituted succinic acid or anhydride (A) or a carboxylic acid, and may be represented by the formulae



or

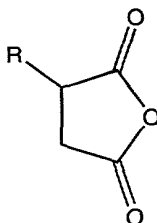


or



15 wherein in each of the above formulae, R is a hydrocarbyl group of about 30 to about 500 carbon atoms at the material has a Mn of 500 to 10,000, and in one embodiment from 500 to 500 carbon atoms and the material has a Mn of about 500 to about 10,000, and in one embodiment about 1000, and in one embodiment from about 1000 to about 5000, and in one embodiment from about 1000 to about 3000.

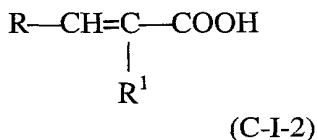
20 In a one embodiment, the acylating agent (C)(I) is a hydrocarbyl-substituted succinic acid and may be derived from the reaction of water with the corresponding succinic anhydride



The carboxylic acids may also be derived from other acylating agent such a carboxylic acid anhydrides, acids, esters, amides, nitriles via reactions well known to those skilled in the art.

In one embodiment, the carboxylic acid or the acylating agent (C)(I) used to prepare the carboxylic acid is made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to about 20 carbon atoms, exclusive of the carboxyl based groups, with one or more olefin polymers containing at least about 20 carbon atoms, as described more fully hereinafter.

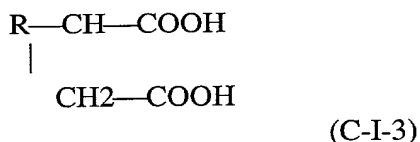
The alpha-beta olefinically unsaturated carboxylic acids may be either monobasic or polybasic in nature. Exemplary of the monobasic alpha-beta olefinically unsaturated carboxylic acids include the carboxylic acids corresponding to the formula



wherein in formula (C-I-2), R is hydrogen, or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R¹ is hydrogen or a lower alkyl group. The total number of carbon atoms in R and R¹ should not exceed about 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinically unsaturated carboxylic acids include acrylic acid; methacrylic acid; cinnamic acid; crotonic acid; 3-phenyl propenoic acid; alpha, and beta-decenoic acid. The polybasic acids are preferably dicarboxylic, although tri- and tetracarboxylic acids can be used. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid.

Reactive equivalents of the alpha-beta olefinically unsaturated carboxylic acid reagents include the anhydride, ester or amide functional derivatives of the foregoing acids. A preferred alpha-beta olefinically unsaturated carboxylic acid is maleic anhydride.

In the preferred embodiment, the acylating agent (C)(I) of this invention is a hydrocarbyl-substituted succinic acid represented correspondingly by the formulae



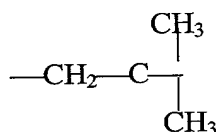
5 wherein in formula (C-I-3), R is hydrocarbyl group of about 30 to about 500 carbon atoms and the material has a Mn of 500 to 10,000, and in one embodiment from 1000 to 5000. The production of such hydrocarbyl-substituted succinic acids or anhydrides via alkylation of maleic acid or anhydride or its derivatives with a halohydrocarbon or via reaction of maleic acid or anhydride with an olefin polymer having a terminal double bond is well known to those of skill in the art and need not be discussed in detail herein.

10 The hydrocarbyl group "R" of the substituted succinic acids and anhydrides of formula (C-I-3) can thus be derived from olefin polymers or chlorinated analogs thereof. The olefin monomers from which the olefin polymers are derived are polymerizable olefin monomers characterized by having one or more ethylenic unsaturated groups. They can be monoolefinic monomers such as ethylene, propylene, butene-1, isobutene and octene-1 or polyolefinic monomers (usually di-olefinic monomers such as butadiene-1,3 and isoprene). Usually these monomers are terminal olefins, that is, olefins characterized by the presence of the group $>\text{C}=\text{CH}_2$. However, certain internal olefins can also serve as monomers (these are sometimes referred to as medial olefins). When such medial olefin monomers are used, they normally are employed in combination with terminal olefins to produce olefin polymers that are interpolymers. Although, the hydrocarbyl substituents may also include aromatic groups (especially phenyl groups and lower alkyl and/or lower alkoxy-substituted phenyl groups such as para(tertiary-butyl)-phenyl groups) and alicyclic groups such as would be obtained from polymerizable cyclic olefins or alicyclic-substituted polymerizable cyclic olefins, the hydrocarbyl-based substituents are usually free from such groups. Nevertheless, olefin polymers derived from such interpolymers of both 1,3-dienes and styrenes such as butadiene-1,3 and styrene or para-(tertiary butyl) styrene are exceptions to this general rule.

25 Generally the olefin polymers are homo- or interpolymers of terminal hydrocarbyl olefins of about 2 to about 30 carbon atoms, and in one embodiment about 2 to about 16 carbon atoms. A more typical class of olefin polymers is selected from that group consisting of homo- and interpolymers of terminal olefins of 2 to about 6 carbon atoms, and in one embodiment 2 to about 4 carbon atoms.

Specific examples of terminal and medial olefin monomers that can be used to prepare the olefin polymers from which the hydrocarbyl-based substituents are derived include ethylene, propylene, butene-1, butene-2, isobutene, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, pentene-2, propylene tetramer, diisobutylene, isobutylene trimer, butadiene-1,2, butadiene-1,3, pentadiene-1,2, pentadiene-1,3, isoprene, hexadiene-1,5, 2-chlorobutadiene-1,3, 2-methylheptene-1, 3-cyclohexylbutene-1, 3,3-dimethylpentene-1, styrenedivinylbenzene, vinyl-acetate allyl alcohol, 1-methylvinylacetate, acrylonitrile, ethyl acrylate, ethylvinylether and methyl-vinylketone. Of these, the purely hydrocarbyl monomers are more typical and the terminal olefin monomers are especially typical.

In one embodiment, the olefin polymers are polyisobutylenes such as those obtained by polymerization of a C₄ refinery stream having a butene content of about 35 to about 75% by weight and an isobutene content of about 30 to about 60% by weight in the presence of a Lewis acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutylenes generally contain predominantly (that is, greater than about 50 percent of the total repeat units) isobutene repeat units of the configuration

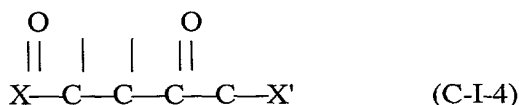


In one embodiment, the hydrocarbyl group R is a polyisobutene group having an average of about 30 to about 500 carbon atoms and a Mn of about 500 to 10,000, and in one embodiment from about 1000 to 5000, and in one embodiment from about 1000 to 3000.

Gel permeation chromatography (GPC) (also known as size exclusion chromatography (SEC)) is a method that can provide both weight average and number average molecular weights as well as the entire molecular weight distribution of polymers. For purposes of this invention, a series of fractionate polymers of isobutene (isobutylene) is used as the calibration standard in the GPC. The techniques for determining number average molecular weight (Mn) and weight average molecular weight (Mw) of polymers are well known and are described in numerous books and articles. For example, methods for the determination of Mn and molecular weight distribution of polymers is described in W.W. Yan, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography," J. Wiley & Sons, Inc., 1979.

In addition to being described in terms of carbon numbers, the polyolefin substituents of the hydrocarbyl-substituted succinic acids and anhydrides of this invention can also be described in terms of their number average and/or weight average molecular weights. An approximate method to convert the number average molecular weight of the polyolefin to number of carbon atoms is to divide the number average molecular weight by 14.

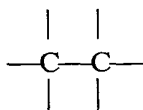
The olefin polymer can be any olefin polymer that has been described hereinbefore in relation to substituent "R" in formula (C-I-3) above. The "succinic groups" are those groups characterized by the structure



wherein in structure (C-I-4), X and X' are the same or different provided that at least one of X and X' is such that the substituted succinic acylating agent can function as a carboxyl acylating agent.

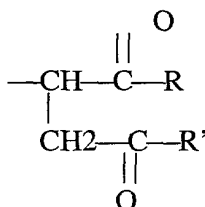
Thus, X and/or X' is usually -OH, -O-hydrocarbyl, -)-M⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, -Br, and together, X and X' can be -O- so as to form the anhydride. The specific identity of any X or X' group which is not one of the above is not critical so long as its presence does not prevent the remaining group from entering into acylation reactions. Preferably, however, X and X' are each such that both carboxyl functions of the succinic group (i.e., both -C(O)X and -C(O)X') can enter into acylation reactions.

One of the unsatisfied valences in the grouping



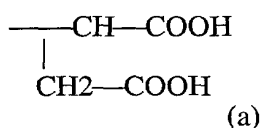
of formula (C-I-4) forms a carbon-carbon bond with a carbon atom in the hydrocarbyl substituent group. While other such unsatisfied valence may be satisfied by a similar bond with the same or different substituent group, all but the said one such valence is usually satisfied by hydrogen; i.e., -H.

In one embodiment, the succinic groups correspond the formula

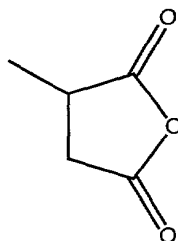


(C-I-5)

wherein in formula (C-I-5), R and R' are each independently selected from the group consisting of -OH, -Cl, -O-lower alkyl, and when taken together, R and R' equal -O-. In the latter case, the succinic group is a succinic anhydride group. All the succinic groups in a particular succinic acylating agent need not be the same, but they can be the same. In one embodiment, the succinic groups correspond to



or

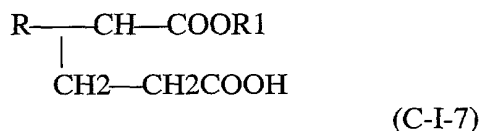


(C-I-6)

or mixtures of (C-I-6)(a) and (C-I-6)(b). Providing hydrocarbyl-substituted succinic acylating agents wherein the succinic groups are the same or different is within the ordinary skill of the art and can be accomplished through conventional procedures such as treating the hydrocarbyl substituted succinic acylating agents themselves (for example, hydrolyzing the anhydride to the free acid) and/or selecting the appropriate maleic or fumaric reactants.

Partial esters of the succinic acids or anhydrides can be prepared simply by the reaction of the acid or anhydride with an alcohol or phenolic compound. Particularly useful are the lower alkyl and alkenyl alcohols such as methanol, ethanol, allyl alcohol, propanol, cyclohexanol, etc. Esterification reactions are usually promoted by the use of alkaline

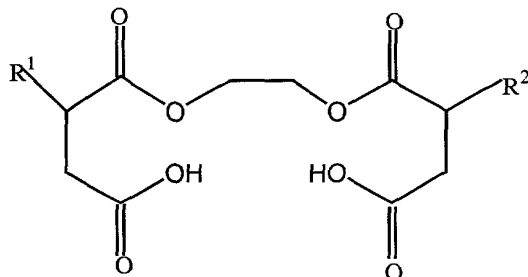
catalysts such as sodium hydroxide or alkoxide, or an acidic catalyst such as sulfuric acid or toluene sulfonic acid. A partial ester can be represented by the formula



wherein in formula (C-I-7), R is a hydrocarbyl group; and R¹ is a hydrocarbyl group, typically a lower alkyl group. In one embodiment, component (C) of the present invention includes the salt compositions of U.S. Patent 5,047,175 ("the '175 patent), except for those salt compositions of the '175 patent which are derived from reacting alkali metal, alkaline earth metal, alkali metal compound, or alkaline earth metal compounds (which fall within components (A)(II) and (B)(II) of the '175 patent). Thus in one embodiment of the present invention, component (C)(I) is made by coupling a) at least one polyisobutene substituted succinic acid or anhydride, the polyisobutene substituent of said succinic acid or anhydride having about 50 to about 200 carbon atoms, and in one embodiment about 50 to about 150, and in one embodiment about 70 to about 100 carbon atoms; and b) at least one hydrocarbyl-substituted succinic acid or anhydride, the hydrocarbyl substituent of said succinic acid or anhydride having up about 8 to about 25 carbon atoms, and in one embodiment from about 10 to about 20 carbon atoms, and in one embodiment about 16 carbon atoms; by (c) at least one coupling agent having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group.

The coupling agent includes those components described under component (C) of the '175 patent, including polyamines, polyols, and hydroxyamines. In one embodiment, the coupling agent of the present invention is ethylene glycol.

In one embodiment the acylating agent (C)(I) comprises at least one compound represented by the formula



wherein R^1 is a polyisobutene group of about 35 to about 300 carbon atoms and R^2 is a hydrocarbyl group of about 10 to 20 carbon atoms. This compound can be seen as the result of coupling a R^1 substituted succinic acid or anhydride with an R^2 substituted succinic acid or anhydride by the coupling agent ethylene glycol.

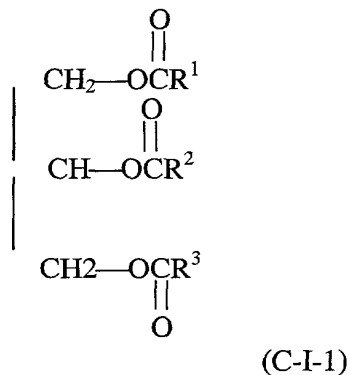
In addition to the methods described in the '753 patent and in EP 0 561 600 A2 for the preparation of the acylating agents of this invention, such as the one step, two step and direct alkylation procedures, the acylating agents of the present invention can also be made via a direct alkylation procedure that does not use chlorine. Polyisobutene-substituted succinic anhydride produced by such a process is available from Texaco under the name TLA™-629C.

The Carboxylic Acid (C)(II)

The acylating agent (C)(II) of this invention includes carboxylic acids and their reactive equivalents such as acid halides and anhydrides.

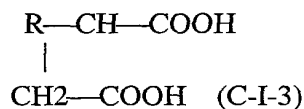
In one embodiment, the carboxylic acid is a monocarboxylic acid of about 1 to about 35 carbon atoms, and in one embodiment about 16 to 24 carbon atoms. Examples of these monocarboxylic acids include lauric acid, oleic acid, isostearic acid, palmitic acid, stearic acid, linoleic acid, arachidic acid, gadoleic acid, behenic acid, erucic acid, tall oil fatty acids and lignoceric acid. These acids may be saturated, unsaturated, or have other functional groups, such as hydroxyl groups, as in 12-hydroxy stearic acid, from the hydrocarbyl backbone.

These carboxylic acids can also be obtained from triglycerides represented by the formula



wherein in formula (C-I-1), R^1 , R^2 and R^3 are independently hydrocarbyl groups such that the total number of carbon atoms in the triglycerides ranges from about 12 to about 500. These triglycerides can be converted into monocarboxylic acid by methods well known to those skilled in the art. The carboxylic acids may be derived from other acylating agent such as carboxylic acid anhydrides, acids, esters, amides, and nitriles via reactions well known to those skilled in the art.

In one embodiment, the carboxylic acid (C)(II) of this invention is a hydrocarbyl-substituted succinic acid represented correspondingly by the formula

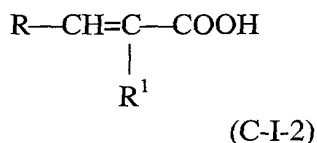


wherein in formula (C-I-3), R is hydrocarbyl group of about 12 to about 35 carbon atoms, and in one embodiment from about 12 to about 30, and in one embodiment from about 16 to about 24 and in one embodiment from about 26 to about 35. The production of such hydrocarbyl-substituted succinic acids or anhydrides via alkylation of maleic acid or anhydride or its derivatives with a halohydrocarbon or via reaction of maleic acid or anhydride with an olefin polymer having a terminal double bond is well known to those of skill in the art and need not be discussed in detail herein.

In one embodiment, the carboxylic acid (C)(II) or the acylating agent used to prepare carboxylic acid (C)(II) is made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to about 20 carbon atoms, exclusive of the carboxyl

based groups, with one or more olefin polymers containing at least about 16 carbon atoms, as described more fully hereinafter.

The alpha-beta olefinically unsaturated carboxylic acids may be either monobasic or polybasic in nature. Exemplary of the monobasic alpha-beta olefinically unsaturated carboxylic acids include the carboxylic acids corresponding to the formula



wherein in formula (C-I-2), R is hydrogen, or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R¹ is hydrogen or a lower alkyl group. The total number of carbon atoms in R and R¹ should not exceed about 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinically unsaturated carboxylic acids include acrylic acid; methacrylic acid; cinnamic acid; crotonic acid; 3-phenyl propenoic acid; alpha, and beta-decenoic acid. The polybasic acids are preferably dicarboxylic, although tri- and tetracarboxylic acids can be used. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid.

Reactive equivalents of the alpha-beta olefinically unsaturated carboxylic acid reagents include the anhydride, ester or amide functional derivatives of the foregoing acids.

A preferred alpha-beta olefinically unsaturated carboxylic acid is maleic anhydride.

The hydrocarbonyl group R of the substituted succinic acids and anhydrides of formula (C-I-3) can thus be derived from olefin polymers or chlorinated analogs thereof. The olefin monomers from which the olefin polymers are derived are polymerizable olefin monomers characterized by having one or more ethylenic unsaturated groups. They can be monoolefinic monomers such as ethylene, propylene, butene-1, isobutene and octene-1 or polyolefinic monomers (usually di-olefinic monomers such as butadiene-1,3 and isoprene). Usually these monomers are terminal olefins, that is, olefins characterized by the presence of the group >C=CH₂. However, certain internal olefins can also serve as monomers (these are sometimes referred to as medial olefins). When such medial olefin monomers are used, they normally are employed in combination with terminal olefins to produce olefin polymers that are interpolymers. Although, the hydrocarbonyl substituents may also include aromatic groups (especially phenyl groups and lower alkyl and/or lower alkoxy-substituted phenyl groups such

as para(tertiary-butyl)-phenyl groups) and alicyclic groups such as would be obtained from polymerizable cyclic olefins or alicyclic-substituted polymerizable cyclic olefins, the hydrocarbyl-based substituents are usually free from such groups. Nevertheless, olefin polymers derived from such interpolymers of both 1,3-dienes and styrenes such as butadiene-1,3 and styrene or para-(tertiary butyl) styrene are exceptions to this general rule.

Generally the olefin polymers are homo- or interpolymers of terminal hydrocarbyl olefins of about 2 to about 30 carbon atoms, and in one embodiment about 2 to about 16 carbon atoms. A more typical class of olefin polymers is selected from that group consisting of homo- and interpolymers of terminal olefins of 2 to about 6 carbon atoms, and in one embodiment 2 to about 4 carbon atoms.

Specific examples of terminal and medial olefin monomers that can be used to prepare the olefin polymers from which the hydrocarbyl-based substituents are derived include ethylene, propylene, butene-1, butene-2, isobutene, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, pentene-2, propylene tetramer, diisobutylene, isobutylene trimer, butadiene-1,2, butadiene-1,3, pentadiene-1,2, pentadiene-1,3, isoprene, hexadiene-1,5, 2-chlorobutadiene-1,3, 2-methylheptene-1, 3-cyclohexylbutene-1, 3,3-dimethylpentene-1, styrenedivinylbenzene, vinyl-acetate allyl alcohol, 1-methylvinylacetate, acrylonitrile, ethyl acrylate, ethylvinylether and methyl-vinylketone. Of these, the purely hydrocarbyl monomers are more typical and the terminal olefin monomers are especially typical.

In the preferred embodiment, the ratio of the first acylating agent (C)(I), to the second acylating agent (C)(II) in the water-blended fuel is in the range of about 9:1 to about 1:9; in another embodiment in the range of about 5:1 to about 1:5; and in another embodiment in the range of about 1:3 to about 3:1.

Component (C)(III)

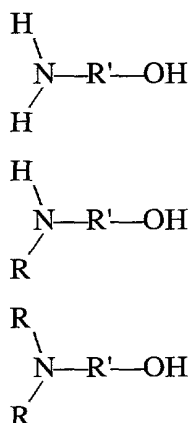
Component (C)(III) of the present invention includes ammonia and/or at least one amine. The amines useful for reacting with the acylating agent (C)(I) of this invention include monoamines, polyamines, or mixtures of these. These amines are described in detail in the '753 patent.

The monoamines have only one amine functionality whereas the polyamines have two or more. The amines can be primary, secondary or tertiary amines. The primary amines are characterized by the presence of at least one -NH_2 group; the secondary by the presence of at

least one H—N< group. The tertiary amines are analogous to the primary and secondary amines with the exception that the hydrogen atoms in the —NH₂ or H—N< groups are replaced by hydrocarbyl groups. Examples of primary and secondary monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, 5 cocoamine, stearylamine, laurylamine, methylaurtylamine, oleylamine, N-methylocylamine, dodecylamine, and octadecylamine. Suitable examples of tertiary monoamines include trimethylamine, triethylamine, tripropyl amine, tributylamine, monomethyldimethyl amine, monoethyldimethylamine, dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl amine, dimethylheptyl amine, and dimethyloctyl amine.

10 In one embodiment, the amines (C)(II) are hydroxyamines. These hydroxyamines can be primary, secondary, or tertiary amines. Typically, the hydroxamines are primary, secondary or tertiary alkanolamines, or mixture thereof.

Such amines can be represented, respectfully, by the formulae:



and mixtures of two or more thereof; wherein in the above formulae each R is independently a hydrocarbyl group of 1 to about 8 carbon atoms, or a hydroxyl-substituted hydrocarbyl group of 2 to about 8 carbon atoms and each R' independently is a hydrocarbylene (i.e., a 35 divalent hydrocarbyl) group of 2 to about 18 carbon atoms. The group —R'—OH in such formulae represents the hydroxyl-substituted hydrocarbylene group. R' can be an acyclic, alicyclic, or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. When two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond 40 or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered

ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R is independently a lower alkyl group of up to seven carbon atoms.

- 5 Suitable examples of the above hydroxyamines include mono-, di-, and triethanolamine, dimethylethanolamine (N,N-dimethylethanolamine), diethylethanol-amine, (N,N-diethylethanolamine), di-(3-hydroxyl propyl) amine, N-(3-hydroxyl butyl) amine, N-(4-hydroxyl butyl) amine and N,N-di-(2-hydroxyl propyl) amine.

Preparation of carboxylic acids from corresponding succinic anhydrides.

- 10 In the preferred embodiment, the acylating agents (C)(I) and (C)(II) are carboxylic acids. If either or both of carboxylic acids (C)(I) and (C)(II) are polycarboxylic acids, those acids can be derived from the corresponding succinic anhydrides by a hydrolysis reaction with water such that the succinic acids are the major products. A minor amount of the succinic anhydride may remain unreacted. Typically, one or more of components (C)(I) and one or more of components (C)(II) are mixed together with an appropriate amount of water (1 equivalent to 10 equivalents, more preferably 1 equivalent to 3 equivalents), and heated to a temperature in the range of from about 20°C to about 100°C, preferably from about 50°C to about 95°C, more preferably 80°C to 95°C; optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, until the desired product has formed.

20 **Reaction of Carboxylic acids (C)(I) and (C)(II) and the Amine (C)(III)**

- The carboxylic acids (C)(I) and (C)(II) are converted into amine carboxylate salts by reaction with ammonia, amine (C)(III), or mixtures thereof. In one embodiment, (C)(III) is a hydroxylamine. In one embodiment, 0.5 to 3.0 equivalents of amine is charged per one acid group of (C)(I) or (C)(II) in preparing the desired salts. More preferably, the amine is charged at 0.5 to 2.0 equivalents per acid group, more preferably, the amine is charged at 0.8 to 1.2 equivalents per acid group. This reaction is carried out at temperatures from about 0°C to about 100°C, more preferably from about 20°C to about 60°C. Typically the ingredients (the acids and the amine(s)) are mixed together at room temperature with no external heating.

- In the disclosed invention, the acylating agent (C)(I) is a succinic acid, and it is reacted with water to prepare a poly(isobutenyl)-substituted succinic acid. In one embodiment the polyisobutylene succinic acid or anhydride has a molecular weight in the

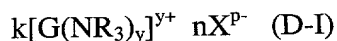
range of about 1000 Mn to about 10,000 Mn, and in another embodiment about 1000 Mn to about 5000 Mn, and in another embodiment about 1500 Mn to about 3000 Mn. This poly(isobutenyl) succinic acid is then reacted with an amine. Preferred amines include but are not limited to alkanolamines and the like. A preferred alkanolamine is diethylamino ethanol. This reaction gives a product that is a disalt, also described as a succinate salt. In the preferred embodiment, the emulsifier is prepared by charging from about 0.2 to about 3.0 eq amine per equivalent of carboxylic acid, more preferred about 0.5 to about 2.0 eq amine per equivalent of carboxylic acid, and more preferred about 0.8 to about 1.2 eq amine per equivalent carboxylic acid.

In one embodiment, component (C)(II) is made by reacting an oleic acid with N,N-diethylamino ethanol in a molar ratio of about 0.2 to about 3.0 eq amine per equivalent of carboxylic acid, more preferred about 0.5 to about 2.0 eq amine per equivalent of carboxylic acid, and more preferred about 0.8 to about 1.2 eq amine per equivalent carboxylic acid. This reaction product is a carboxylate salt.

The Water-Soluble Salt (D)

Another component of the present composition is a water-soluble, ashless (i.e. metal-free), halogen-, boron-, and phosphorus-free amine salt, distinct from component (C). The term "amine" as used herein includes ammonia. Particularly useful are the amines or ammonium salts such as ammonium nitrate, ammonium acetate, methyl ammonium nitrate, methyl ammonium acetate, ethylene diamine diacetate, urea nitrate, urea, guanidiniumnitrate, and mixtures thereof.

In one embodiment, the amine salt (D) is represented by the formula



Wherein in formula (D-I), G is hydrogen, or an organic neutral radical of 1 to about 8 carbon atoms, and in one embodiment 1 to 2 carbon atoms, having a valence of y; each R independently is hydrogen or a hydrocarbyl group of 1 to about 10 carbon atoms, and in one embodiment 1 to about 5 carbon atoms, and in one embodiment 1 to 2 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently at least 1, provided that when G is H, y is 1, and further provided that the sum of the positive charge ky^+ is equal to the sum of the negative charge nX^{p-} , such that the amine salt (D) is electrically neutral. In one embodiment, (D) is a hydrocarbyl or hydrocarbylene group of 1 to about 5 carbon, and in one

embodiment 1 to 2 carbon atoms. In one embodiment, X^{y-} is a nitrate ion ($y=1$); in one embodiment it is an acetate ion ($y=1$). Suitable examples of the amine salt include ammonium nitrate ($NH_3.HNO_3$), ammonium acetate ($NH_3.HOC(O)CH_3$), methylammonium nitrate ($CH_3NH_2.HNO_3$), methylammonium acetate ($CH_3NH_2.HOOCCH_3$), ethylene diamine diacetate ($H_2NCH_2CH_2NH_2.2HOOCCH_3$), urea nitrate ($H_2NC(O)NH_2.HNO_3$), and urea dintrate ($H_2NC(O)NH_2.2HNO_3$).

As an illustration of formula (D-I), ethylene diamine diacetate can be written in its ionic form as



In this case, in formula (D-I), G is $—CH_2CH_2—$; R is hydrogen; y is 2; n is 2; p is 1; and X^p- is $CH_3CO_2^-$

In one embodiment, the amine salt (D) of the present composition functions as an emulsion stabilizer, i.e., it acts to stabilize the present emulsified water-blended fuel composition. Compositions with the amine salt (D) have longer stability as emulsions than the compositions without the amine salt (D).

In one embodiment, the amine salt (D) functions as a combustion improver. A combustion improver is characterized by its ability to increase the mass burning rate of water-blended fuel composition. It is known that the presence of water in fuels reduces the power output of an internal combustion engine. The presence of a combustion improver has the effect of improving the power output of an engine. The improved power output of the engine can often be seen in a plot of mass burning rate versus crank angle (which angle corresponds to the number of degrees of revolution of the crankshaft which is attached to the piston rod, which in turn is connected to pistons). One such plot is shown in Figure 2, which is discussed further under Examples below. The mass burning rate will be higher for a fuel with a combustion modifier than for a fuel lacking the combustion modifier. This improved power output caused by the presence of a combustion improver is to be distinguished from improvement in ignition delay caused by a cetane improver. Although some cetane improvers may function as a combustion improver, and some combustion improvers as cetane improvers, the actual performance characteristics or effects of combustion improvement are clearly distinct from improvements in ignition delay. Improving ignition delay generally relates to changing the onset of combustion (i.e. they will affect where on the x-axis of Fig. 1

the peak mass burning rate will occur) whereas improving the power output relates to improving the peak cylinder pressure (i.e., the amplitude of the peak mass burning rate on the y-axis of Fig. 1.)

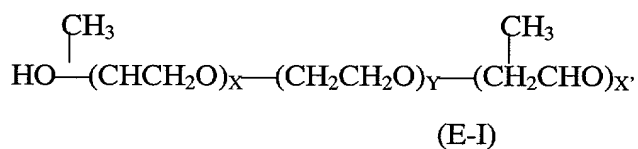
The amine salt (D) is present at a level of about 0.001 to about 15%, in one embodiment from about 0.001 to about 1%, in one embodiment about 0.05 to about 5%, in one embodiment about 0.5 to about 3%, and in one embodiment about 1 to about 10% by weight of the emulsified water-blended fuel composition.

The Cosurfactants

In addition to the presence of component (C) as an emulsifier, the present composition can also contain other emulsifiers, which may be present as cosurfactants. These emulsifiers/cosurfactants include but are not limited to ionic or nonionic compounds, having a hydrophilic lipophilic balance (HLB) in the range of about 1 to about 40, and in one embodiment about 4 to about 15. Examples of these emulsifiers are disclosed in McCutcheon's Emulsifiers and Detergents, 1993, North American & International Edition.

Some generic examples include alkanolamides, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units (e.g., Pluronic™ s), carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, glycerol esters, glycol esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkyl phenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

In one embodiment, the cosurfactant is a poly(oxyalkene) compound, and in one embodiment, the polyoxyalkylene compound is a copolymer of ethylene oxide and propylene oxide copolymer. In one embodiment, this copolymer is a triblock copolymer represented by the formula



wherein in formula (E-I), x and x' are the number of repeat units of propylene oxide and y is the number of repeat units of ethylene oxide, as shown in the formula. This triblock copolymer is available from BASF Corporation under the name PLURONIC™ R surfactants. In one embodiment, the triblock copolymer has a number average molecular weight of about 1800 to about 3000. In one embodiment, the triblock copolymer has a number average molecular weight of about 2150, is a liquid at 20°C, having a melt/pour point of about -25°C, has Brookfield viscosity of 450 cps, and has surface tensions (25°C) at 0.1, 0.01, and 0.001% concentration of about 41.9, 44.7, and 46.0 dynes/cm respectively. It is available under the name PLURONIC™ 17R2. In one embodiment, the triblock copolymer has a number average molecular weight of about 2650, is a liquid at 20°C, having a melt/pour point of about -18°C, has Brookfield viscosity of 600 cps, and has surface tensions (25°C) at 0.1, 0.01, and 0.001% concentration of about 44.1, 44.5, and 51.4 dynes/cm respectively. It is available under the name PLURONIC™ 17R4.

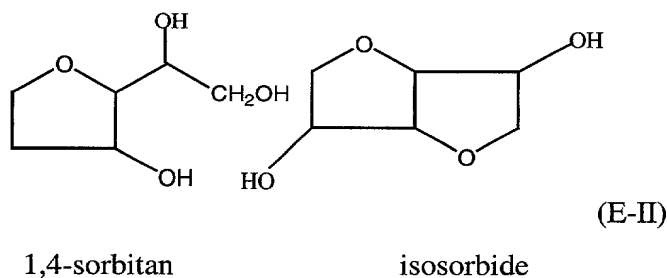
In one embodiment, the poly(oxyalkylene) compound is an alcohol ethoxylate represented by the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ wherein R is a hydrocarbyl group of 8 to 30 carbon atoms, and in one embodiment about 8 to about 20, and in one embodiment about 10 to about 16 carbon atoms; and n ranges from about 2 to about 100, and in one embodiment about 2 to about 20, and in one embodiment about 2 to about 10. In one embodiment R is nonylphenyl, and in one embodiment, R is nonylphenyl and n is about 4. It is available from Rhone-Poulenc, under the name IGEPAL™ CO-430. It has about 44% ethylene oxide, has an HLB value of about 8.8. It is an aromatic odor, is pale yellow liquid, having a density at 25°C of 1.02, viscosities at 25°C and 100°C of about (160-260) and (8-10) respectively; solidification point of -21 to 2; and a pour point of -16 to 2°F. In one embodiment, R is nonylphenyl and n is about 6. It is available from Rhone-Poulenc, under the name IGEPAL™ CO-530. It has about 54% ethylene oxide, has an HLB value of about 10.8. It is an aromatic odor, is pale yellow liquid, having a density at 25°C of 1.04, viscosities at 25°C and 100°C of

about (180-280) and (10-12) respectively; solidification point of -23 to 2°F ; and a pour point of -18 to 2°F .

In one embodiment, R in the above alcohol ethoxylate is a linear C_{9-11} alkyl group and n ranges from about 2 to about 10, and in one embodiment from about 2 to about 6. These alcohol ethoxylates are available from Shell International Petroleum Company under the name NEODOL[™] alcohol ethoxylates. In one embodiment, n is about 2.7. It is available under the name NEODOL[™] 91-2.5. It has a number average molecular weight of about 281, an ethylene oxide content of about 42.3% by weight, a melting range of about -31 to -2°F , a specific gravity (77°F) of about 0.925, viscosity at 100°F of about 12cSt, a hydroxyl number of about 200 mg KOH/g, and an HLB number of about 8.5. In one embodiment, n is about 8.2. It is available under the name NEODOL[™] 91-8. It has a number average molecular weight of about 519, an ethylene oxide content of about 69.5% by weight, a melting range of about 45°F to 68°F , a specific gravity (77°F) of about 1.008, viscosity at 100°F of about 39 cSt, a hydroxyl number of about 108 mg KOH/g, and an HLB number of about 8.5.

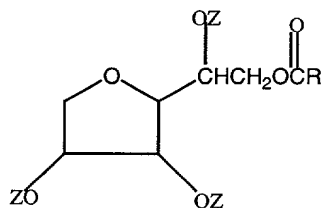
In one embodiment the cosurfactant comprises at least one sorbitan ester.

The sorbitan esters include sorbitan fatty acid esters wherein the fatty acid component of the ester comprises a carboxylic acid of about 10 to about 100 carbon atoms, and in one embodiment about 12 to about 24 carbon atoms. Sorbitan is a mixture of anhydrosorbitols, principally 1,4-sorbitan and isosorbide:



Sorbitan, (also known as monoanhydrosorbitol, or sorbitol anhydride) is a generic name for anhydrides derivable from sorbitol by removal of one molecule of water. The sorbitan fatty acid esters of this invention are a mixture of partial esters of sorbitol and its

anhydrides with fatty acids. These sorbitan esters can be represented by the structure below which may be any one of a monoester, diester, triester, tetraester, or mixtures thereof.

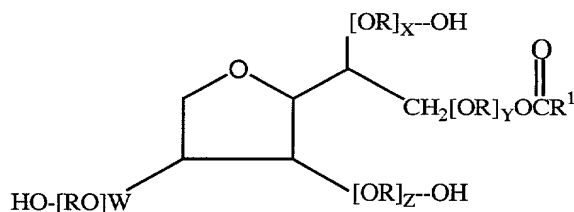


(E-III)

In formula (E-III), each Z independently denotes a hydrogen atom or C(O)R-, and each R mutually independently denotes a hydrocarbyl group of about 9 to about 99 carbon atoms, more preferably about 11 to about 23 carbon atoms. Examples of sorbitan esters include sorbitan stearates and sorbitan oleates, such as sorbitan stearate (i.e., monostearate), sorbitan distearate, sorbitan tristearate, sorbitan monooleate and sorbitan sesquioleate.

Sorbitan esters are available commercially under the names Spans[™] and Arlacels[™] from ICI.

The sorbitan esters also include polyoxyalkylene sorbitan esters wherein the alkylene group has about 2 to about 30 carbon atoms. These polyoxyalkylene sorbitan esters can be represented by the structure



(E-IV)

wherein in formula (E-IV), each R independently is an alkylene group of about 2 to about 30 carbon atoms; R¹ is a hydrocarbyl group of about 9 to about 99 carbon atoms, more preferably about 11 to about 23 carbon atoms; and w, x, y and z represent the number of repeat oxyalkylene units. For example ethoxylation of sorbitan fatty acid esters leads to a series of more hydrophilic surfactants, which is the result of hydroxy groups of sorbitan reacting with ethylene oxide. One principal commercial class of these ethoxylated sorbitan esters are those containing about 2 to about 80 ethylene oxide units, and in one embodiment from about 2 to

about 30 ethylene oxide units, and in one embodiment about 4, in one embodiment about 5, and in one embodiment about 20 ethylene oxide units. They are available from Calgene Chemical under the name POLYSORBATE™ and from ICI under the name TWEEN™.

Typical examples are polyoxyethylene (hereinafter "POE") (20) sorbitan tristearate (Polysorbate 65; Tween 65), POE (4) sorbitan monostearate (Polysorbate 61; Tween 61), POE (20) sorbitan trioleate (Polysorbate 85; Tween 85), POE (5) sorbitan monooleate (Polysorbate 81; Tween 81), and POE (80) sorbitan monooleate (Polysorbate 80; Tween 80). As used in this terminology, the number within the parentheses refers to the number of ethylene oxide units present in the composition.

In one embodiment, the cosurfactant comprises at least one fatty acid diethanolamide. The fatty acid diethanolamides are 1:1 fatty acid diethanolamides made by reacting a fatty acid with diethanolamide in a 1:1 mole ratio under amide forming conditions. These 1:1 fatty acid diethanolamides are available from Witco Corporation under the name SCHERCOMID™. The fatty acids used to make these 1:1 fatty acid diethanolamides may be monocarboxylic fatty acids or they may be derived from natural oils (such as triglycerides). Useful fatty acids and their sources include lauric acid, myristic acid, coconut acid, coconut oil, oleic acid, tall oil fatty acid, linoleic acid, soybean oil, apricot kernel oil, wheat germ oil, and mixtures thereof. In one embodiment, the fatty acid diethanolamide is derived from oleic acid. It is available commercially under the name SCHERCOMID™ SO-A also referred to as Oleamide DEA. It is a clear amber liquid, has a maximum acid value of about 5, an alkali value of about 40-60, and contains a minimum of 85% amide.

The cosurfactant when present is present in an emulsifying amount, i.e., it is present in a quantity sufficient to maintain the present composition as an emulsion. In one embodiment, it is present at a level of about 0.005 to about 20%, and in one embodiment from about 0.005 to about 10%, and in one embodiment from about 0.005 to about 1%.

The Organic Nitrate Cetane Improver

In one embodiment of the present invention, the present composition further comprises at least one organic cetane improver. The organic nitrate cetane improver includes nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Specific examples of nitrate compounds suitable for use in the present invention include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also suitable are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. While not particularly preferred, the nitrate esters of higher alcohol may also be useful. Such higher alcohols tend to contain more than about 10 carbon atoms. Preferred are the alkyl nitrates having from about 5 to about 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

The concentration of the organic nitrate cetane improver in the present composition can be any concentration sufficient to counteract the reduction in cetane number caused by the addition of water in the present water-blended fuel compositions. Generally, addition of water to fuel acts to lower the cetane number of the fuel. As a general rule of thumb, the cetane number of fuel goes down by 1/2 unit per each 1% addition of water. Lowering of cetane number results in ignition delay, which can be counteracted by the addition of cetane enhancers/improvers. Generally, the amount of organic nitrate cetane improver ester will fall in the range of about 0.05% to about 10% and in one embodiment about 0.05% to about 1% by weight of the water-blended fuel composition.

The Alcohol/Antifreeze

In one embodiment of the present invention, the composition further comprises an alcohol. The alcohol is generally an antifreeze agent but may also be a cosolvent or combinations of both. Examples of suitable alcohols and their isomers include, but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol, isopropanol, octanol, butanol, pentanol, hexanol, heptanol, 4-ethoxy butanol and combinations thereof.

The antifreeze can be present at any concentration sufficient to keep the present composition from freezing within the operable temperature range. In one embodiment, it is present at a level of about 0.01% to about 10%, and in one embodiment, about 0.1% to 5% by weight of the water-blended fuel composition.

Specific Embodiment

The following examples demonstrate the advantages of the present invention.

Example 1: Preparation of PIB succinic acid

A 2300 Mn poly(isobutenyl) succinic anhydride (about 9410g, about 6.84 eq C=O) was charged to a 12-liter spherical 4-neck flask equipped with a temperature controller regulating a rheostated heating mantle and a thermocouple in a glass thermowell. The material was stirred at about 45°C and an above-surface N₂ sweep was set at about 1 SCFH (standard cubic feet per hour). The mixture was heated to about 90°C. Deionized water (about 184.8g, about 20.54 equivalents) was then added over about 10 minutes. The mixture was heated at about 90°C for about 2 hours. Infrared analysis showed acid peak at 1714 cm⁻¹ with a slight anhydride or lactone shoulder at 1786 cm⁻¹. The mixture was cooled to about 50°C and discharged.

Example 2: Simultaneous preparation of both salts.

Oleic acid (about 2450g), 2-ethyl hexyl nitrate (about 3420g), and hydrolyzed 2300 molecular weight PIBSA (about 2410g, about 50% active chemical by weight) (from Example 1) was charged to a 12-liter spherical 4-neck flask equipped with a temperature controller monitoring a thermocouple in a glass thermowell. The mixture was stirred at room temperature under a nitrogen flow at about 1 SCFH, and the materials were mixed until homogeneous. Diethylamino ethanol (about 1110g) was charged over 1 hour, and a mild exotherm was observed. The resulting material was a solution of carboxylate salts in 2-ethylhexyl nitrate.

Some illustrative water-blended fuel compositions within the scope of the invention are disclosed Table 1. The amounts are in parts by weight.

TABLE I

Components	Emulsion A	Emulsion B	Emulsion C
Diesel Fuel	77.80	77.51	75.30
Water	20.00	20.00	16.80
Surfactant 1 ¹ (~50% active)	0.526	1.16	0.526
Surfactant 2 ²	0.724	0.382	0.724
2-ethyl hexyl nitrate	0.714	0.714	0.714
Ammonium nitrate	0.12	0.12	0.12
Propylene glycol	0.12	0.12	0.12
Methanol	0	0	5.70

¹This is a biscoxylate salt that is made by reaction of hydrolyzed 2300 molecular weight PIBSA with diethyl ethanolamine.

²This is a carboxylate salt that is made by reacting oleic acid with diethyl ethanolamine.

The emulsions have a milky white appearance. The stability of the emulsion is determined visually by tracking percentage of water-blended fuel composition remaining as a white emulsion at room temperature four weeks after preparation. The percentage of white emulsion and free oil is indicated in the table below:

Components	Emulsion A	Emulsion B	Emulsion C
Free oil	7	9	13
White emulsion	93	91	87

As a point of reference, a baseline surfactant system gives >10% oil and < 90% white emulsions after 4 weeks at room temperature.

This is illustrative of concentrates that can be used to make the water-blended fuel compositions of the invention. The numerical values indicated below are parts by weight.

Components	Concentrate A	Concentrate B
PIB succinic acid ¹	21.94	41.48
Oleic acid	22.24	10.52
Diethylamino ethanol	10.11	6.95
2-ethyl hexyl nitrate	31.04	27.049
54% aqueous ammonium nitrate	9.66	8.56
Propylene glycol	5.00	5.00

¹derived from 2300 molecular weight PIBSA

This demonstrates that the emulsified water-blended fuel compositions using the concentrates disclosed above. In the table below, all numerical values are in parts by weight.

Components	Emulsion A	Emulsion B
Diesel Fuel	79-81	79-81
Water	18-20	18-20
Concentrate A	1.5-3.0	---
Concentrate B	---	1.5-3.0

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.